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Anthropogenic influence on rainwater in the Xi'an City, Northwest China: Constraints from sulfur isotope and trace elements analyses

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ABSTRACT

Sulfur isotopes of sulfate and trace elements in the rain and snow water samples from the Xi'an urban and rural sites were measured from 2007 to 2008 to investigate atmospheric pollution and identify anthropogenic influence on precipitation. The results show that the $\delta^{34}S$ values of SO_4^{2-} ranging from +8.71‰ to +19.05‰ (average +13.41‰, $n = 30$) in the Xi'an urban site and from +4.67‰ to +20.59‰ (average +11.23‰, $n = 31$) in the suburb site are significantly higher with respect to those generally reported for precipitation samples around the world. This indicates a dominant source of coal-burning emissions of SO_2 in the studied precipitation samples due to sulfur in the coal from Northern China having relative high $\delta^{34}S$ value. Trace elements such as Ti, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Cd, Pb, Al and Fe were also analyzed by or Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) in the present study. Enrichment factors related to Si in both crust and loess suggest that most of the studied trace elements have an anthropogenic origin. Only Al, Ti and Fe show a significant loess source. While Cr, Co, Cu and Pb in the precipitation samples from both of the two sampling sites have similar distribution patterns compared to those of local fly ashes mostly originated from coal combustion. Zinc in the precipitation samples appears to be controlled mainly by industrial and/or traffic sources. Both of the trace elements and sulfur isotopic composition indicate that coal combustion is the main source for air pollutants in the Xi'an City and its surrounding regions. The study results also reveal that serious air pollution in the Xi'an City is widely diffused significantly affecting also the adjacent rural area up to 100 km from the city.

1. Introduction

Air pollution has become one of the important environmental pollution problems in China since the 1980s with the rapid economic growth and increase in industrial activity. Trace elements and sulfur are among the major pollutants of the atmosphere. Sulfur is mostly emitted from heavily industrialized areas where fossil fuels are extensively consumed and SO_2 is the major precursor of acid rain (Larssen et al., 1999, 2011; Zhao et al., 1988), while trace elements may be released from coal combustion and industry waste gas. The use of sulfur-containing fossil fuels released about 22 million metric tons of sulfur dioxide into atmosphere in China in 2003 (Larssen et al., 2006). However, due to the predominant use of sulfur-rich coals, acid rain has been one of the serious environmental problems in the south and southwestern of China, which is one of the three big acid rain areas in the world, together with Europe and North America (Larssen et al., 1999, 2011; Zhao et al., 1988). Thus, studies of acid rain in China mostly focused on the southwestern cities such as Chongqing and Guiyang. Few studies of acid rain were reported for cities in north China. On the other hand, due to the widespread presence of alkaline loess and soil within north China having very high acid neutralizing capacity, acidification is considered to be a minor problem in this area (Larssen and Carmichael, 2000; Larssen et al., 2011).

The Xi'an City located at the famous Loess Plateau is one of the largest industrial cities in Northwest China. It is the capital of Shaanxi Province and has a population of 8 million inhabitants. Loess soils cover a vast area in the semi-dry climate region. Annual rainfall in the Xi'an City and its adjacent regions is about 580 mm with a remarkable seasonal variability affected by the continental monsoon. The main precipitations are in the rainy season from July to August every year. Cloud water originates from Pacific air masses in summer while Siberian and Mongolian air masses prevail in winter. Within recent several decades, the Xi'an City was extremely polluted in terms of SO_2. Previous studies on rainwater in the Xi'an district were confined to major ions and Pb (Lu et al., 2011; Xu et al., 2012). Some of researches were on the cities in north China (Xu and Han, 2009; Xu et al., 2009). But up to now, little is known about the source of SO_4^{2-} and dispersion and transport of SO_2 in the Xi'an region. The study on the trace elements determination in the dissolved fraction of the precipitation in the Xi'an City and its surrounding areas has not been reported yet.

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Sulfur isotopic tracing has been an effective way to track the origin of sulfate in precipitations. Intensive researches had been carried out to identify possible sulfur sources of sulfate in atmospheric deposition by using the sulfur isotopic tool (Herut et al., 1995; Mast et al., 2001; Nriagu et al., 1987; Pruett et al., 2004; Puig et al., 2008; Wakshall and Nielsen, 1982; Xiao and Liu, 2002). The main focus of the present study will be the determination of the sources of sulfate and trace elements in precipitation, the identification of the anthropogenic influence on precipitation and the explanation of the diffusion mechanisms of the pollutant in the Xi'an City. The results of the study can also help us to draw up the right plans protecting air environment from pollution caused by human activities.

2. Sampling and analytical methods

The map of the Xi'an City and the sampling locations is presented in Fig. 1. Precipitation samples were collected at two monitoring sites in the Xi'an City (Fig. 1). One is the urban site, located in the campus of Northwest University in a commercial district, and the other is the suburb site which represents rural area located near a small county named Yongshou which is about 90 km northwest of Xi'an urban. Xi'an is an inland city in the interior of China, and the nearest distance from the sea to the study area is more than 900 km. Although the climate and geological conditions are similar, the air pollution caused by human activities differs greatly between the two sampling sites. The urban site reflects the industrial, heavy traffic and high population density characteristics of the city, and the suburb site (Yongshou) shows characteristics of the regional background. Only one national road (G312) is 150 m away from the Yongshou site (Fig. 1).

The precipitation samples were collected every time no matter the amount of rainwater or snow for 1 year from January 2007 to January 2008, and a total of 71 samples were collected. Precipitation samples were collected on the roof of buildings far from pollution point sources. We use PE boxes as the containers. Prior to use, the boxes were cleaned with 4 N HCl solution and rinsed with Milli-Q water, and dried. In most cases, samples of rainfalls were collected from the beginning to the end. Continuous rainfalls occurred 24 h intervals during the period of sampling, so it is easy to distinguish one rainfall event from another. Measurement of pH, electrical conductivity (EC) and amount of precipitation of the samples were performed in-situ.

After collection, precipitation samples were filtered through Millipore membrane filters and the filtrate was separated and stored in two aliquots. One aliquot was frozen at 4 °C for anions, cations and trace elements measurement, while the other aliquot for S isotopic analysis after it was poisoned by $HgCl_2$ solution. Major anions (SO_4^{2-}, NO_3^-, Cl^-) in the samples without acidification were measured using ion chromatograph (DIONEX ICS-90), and major cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Al^{3+}, and Fe^{3+}) and DSi by inductively coupled plasma optical emission spectrometer (Visata MPX ICP-OES) after acidification with ultra-purified nitric. Trace elements were determined by ICP-MS (Thermo X Series) after the same acidification. Reagent and procedural blanks were taken during the rinsing step of the samplers and in analytical process. Concentrations in the blanks were lower than the detection limits of trace elements. The $\delta^{34}S$ analysis of sulfate was preformed on CF-IRMS (IsoPrime JB144). The standard deviation for the $\delta^{34}S$ determination of NBS127 was $\pm 0.2‰$ ($n = 11$). In order to precipitate sulfate as $BaSO_4$ for the S isotope measurement, acidified samples were reacted with excess $BaCl_2$ solution. After 12 h, the mixture was filtered through 0.22 μm acetate membrane filters. The precipitates ($BaSO_4$) on the membrane filters were carefully rinsed with enough Milli-Q water to remove Cl^-, and immediately transferred into crucibles with the membrane filters and combusted at 840 °C for half an hour. The white powder ($BaSO_4$) appeared, and that was decomposed at high temperature to SO_2 in a vacuum line for $\delta^{34}S$ determination, according to the method of Yanagisawa and Sakai (1983).

3. Results and discussion

3.1. pH and major ions

The analytical results are shown in Table 1. The results show that the pH values of the precipitation samples range from 4.37 to 7.75 with an

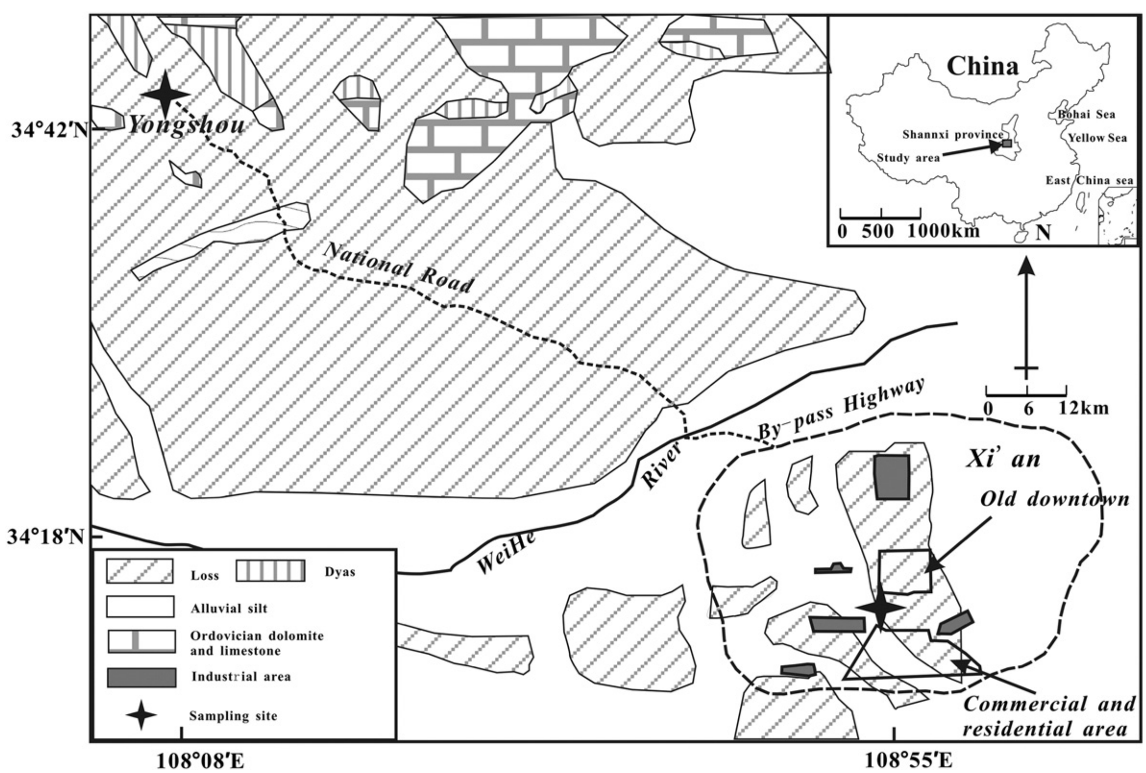

Fig. 1. Map of the Xi'an City and Yongshou site showing the sampling locations.